

Supporting Information for

Interstellar Ice Chemistry Yields Elusive Sulfinothioic Acid (HS(O)SH)

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METHODS

Irradiation Experiments

Each experiment was conducted under ultrahigh vacuum conditions of a few 10^{-11} Torr maintained inside a stainless-steel chamber by two magnetically suspended turbomolecular pumps in series (Osaka, TG1300MUCWB and TG420MCAB) backed by an oil-free scroll pump (XDS35i, BOC Edwards).^[23, 25-26] Ice temperatures of 5 K were achieved utilizing a closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK415E) cooling an oxygen-free high conductivity copper target. A polished silver substrate mounted to the target acted as substrate for each ice mixture. Samples of sulfur dioxide (SO_2 , AirGas, 99.5%), water (H_2O , Sigma Aldrich), deuterium oxide (D_2O , Sigma Aldrich 99.9 atom %), and water- ^{18}O (H_2^{18}O , Sigma Aldrich, 99.9 atom %) were used to prepare the corresponding ices. Once the silver wafer reached 5 K, sulfur dioxide and water were inlet into the stainless-steel chamber *via* two separate glass capillary arrays at partial pressures of 3×10^{-9} Torr for sulfur dioxide and 1×10^{-8} Torr for water. This process of deposition was monitored *in situ* by laser interferometry using a helium-neon laser (CVI Melles Griot, 25-LHP-230, 632.8 nm).^[41] The resulting fringes formed from reflections from the ice surface on the silver substrate were collected with a photodiode. The respective refractive index (n) of the $\text{SO}_2/\text{H}_2\text{O}$ ice was determined to be 1.31 ± 0.02 based on a weighted average of the two individual refractive indexes of the pure ices (SO_2 , 1.36;^[42] H_2O , 1.26)^[43] and then used to calculate the average ice thickness of 1280 ± 60 nm.^[41] For a full list of experiments conducted here refer to Table S1.

After deposition, Fourier Transform Infrared (FTIR) spectra of the ices were collected using a FTIR spectrometer (Bruker, Vertex Neo R) at 4 cm^{-1} resolution (Figure S2, Table S2). The ice composition was calculated using the respective band strengths of SO_2 (ν_1 , $1.47 \times 10^{-17} \text{ cm molecule}^{-1}$)^[44] and H_2O (ν_2 , $1.0 \times 10^{-17} \text{ cm molecule}^{-1}$)^[43] to be an ice ratio of $\text{SO}_2:\text{H}_2\text{O}$ of $1:1.2 \pm 0.2$. These ratios do not directly reflect ice ratios within cold molecular clouds, but were chosen as a prototype system to gauge reactions of SO_2 . Irradiation of the ice was conducted in tandem with FTIR measurements with an electron gun (SPECS, EQ PU-22) producing 5 keV electrons rastered over the sample surface at an angle of incidence of 70° . These electrons reproduce chemical reactions initiated by the secondary electrons produced by galactic cosmic rays (GCRs) penetrating ices on interstellar grains.^[45-46] By simulating the penetration of these electrons into the ice using CASINO v2.42^[47], the penetration depth and dose can be calculated utilizing the respective density of each ice component (SO_2 , 1.343 g cm^{-3} ;^[48] H_2O , 0.97 g cm^{-3} [49]). These simulations result in an average penetration depth of 540 nm which is much smaller than the ice thickness of 1280 nm; thus, penetrating electrons only modify the ice and not the silver wafer. Calculated dose derived from simulations result in $2.5 \text{ eV molecule}^{-1}$ for water and $6.3 \text{ eV molecule}^{-1}$ for SO_2 .

After the irradiation, the ice mixtures were heated from 5 K to 330 K at a rate of 1.0 K min^{-1} in a temperature-programmed desorption (TPD) process. This heating results in the sublimation of the newly formed products and reactants, which were subsequently detected in the gas phase via vacuum ultraviolet (VUV) photoionization reflectron time-of-flight mass spectrometry (PI-ReToF-MS).^[23, 25-26, 50-51] Tunable VUV photons were generated by resonant four-wave mixing in a pulsed noble gas jet (Krypton and Xenon, Table

S3). These experiments use Nd: YAG lasers (Spectra-Physics, Quanta Ray Pro 250-30 and 270-30) to pump two dye lasers (Sirah, Cobra-Stretch), to produce tunable VUV light.^[50-51] For information regarding VUV generation schemes used in these experiments refer to Table S3. The VUV light generated by the noble gas jet was then separated by a biconvex lithium fluoride lens (Korth Kristalle, R = 131 mm) in an off-axis geometry to the center of the lens. Ultimately, this results in a single wavelength of light directed 2.0 mm from the ice surface to ionize subliming molecules during TPD. These ionized molecules are extracted into a ReToF-MS (Jordan TOF Products) and detected with a dual multichannel plate detector. Ion signals were amplified, discriminated, and measured by a multichannel scaler (FAST ComTec, MCS6A) binning signal into 3.2 ns sections and recorded over 2-minute intervals (3600 sweeps).

Computational

Each neutral and cation molecular geometry is optimized with at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory with the MOLPRO 2022 program.^[52-56] The corresponding harmonic frequencies of each geometry provide confirmation of the structure as a minimum and also produces zero-point vibrational energy (ZPVE) corrections which are added to the electronic energies. The relative energies result from differences between the electronic + ZPVE energies for each of the isomers of a single charge. The adiabatic ionization energies are the differences between the total energy of each neutral and corresponding radical-cation. The radical-cation geometry optimizations begin from the optimized neutrals in order to provide clear correlation between neutral and charged species. Additionally, anharmonic B3LYP/aug-cc-pVTZ frequencies are computed for the observed isomer utilizing Gaussian16.^[57-61] For a full list of IEs, relative energies, geometries, vibrational modes and oscillator strengths see Table S4-S7.

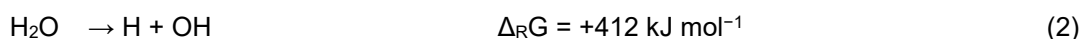
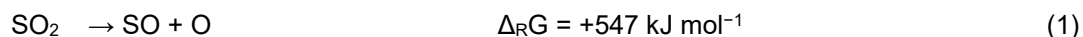
Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was utilized to monitor the emergence of new vibrational modes during irradiation of the SO₂/H₂O ice. The FTIR spectra before irradiation and after irradiation (Figure S2, Table S2) reveals new functional groups associated with non-equilibrium chemical reactions occurring from processing by energetic electrons. The spectrum before the irradiation shows a pristine SO₂/H₂O ice consisting of fundamental vibrational modes of each reagent species. Here, SO₂ is identified by ν_1 (1152 cm⁻¹) and ν_3 (1322 cm⁻¹).^[62] Fundamental vibrational modes of water such as ν_1/ν_3 (3000–3500 cm⁻¹), ν_2 (1650 cm⁻¹), and lattice modes (ν_L , 811 cm⁻¹) are observed.^[43] After the irradiation, several new peaks reveal new irradiation products. Peaks associated with increased intermolecular hydrogen bonding are observed such acidic O-H stretching modes such at 2957 and 2456 cm⁻¹.^[63] The O-H stretching mode at 2456 cm⁻¹ indicates strengthening of the hydrogen-bonding network and is consistent with the presence of sulfur-bearing acidic functionalities within the ice.^[34, 63-66] The emergence of new O-H stretching modes are detected at 3573 and 3502 cm⁻¹ while an S-O-H bending mode is observed at 1131 cm⁻¹.^[63] This bending mode overlaps with S=O symmetric stretches, but this region is also consistent with S-O-H bending vibrations reported for (H₂SO₄), sulfurous acid (H₂SO₃), and the S=O stretching of H₂S₂O.^[5, 65, 67] The increase in hydrogen bonding in the ice along with new O-H stretching and S-O-H bending suggests the

formation of new acidic groups in the ice. A suite of S=O stretching is also observed at 1289, 1253, and 1211 cm^{-1} which correlates to the asymmetric stretching and another set at 1179 and 1136 cm^{-1} corresponding to symmetric stretching. Additionally, S-O stretching is observed by peaks at 1047, 1025, 972, and 949 cm^{-1} .^[63] Additional vibrational analysis was carried out using simulated anharmonic spectra of sulfinothioic acid **1**, HSS(O)H, computed at the B3LYP/aug-cc-pVTZ level, together with isotopically labeled FTIR experiments on $\text{SO}_2/\text{H}_2^{18}\text{O}$ and $\text{SO}_2/\text{D}_2\text{O}$ (Figure S3, Tables S8–S10). The calculations predict the most intense feature of sulfinothioic acid **1** to be an S=O stretching vibration at 1108 cm^{-1} , 1063 cm^{-1} , and 1108 cm^{-1} for HSS(O)H, HSS(^{18}O)H, and DSS(O)D, respectively (Table S10). After irradiation, the FTIR spectra show increased absorption near this region, with the clearest isotope-dependent change observed for the $\text{SO}_2/\text{H}_2^{18}\text{O}$ ice, where features appear at 1086 and 1045 cm^{-1} . These data are consistent with perturbation of sulfur–oxygen vibrational modes upon isotopic substitution and provide additional support for assignments in the S–O–H/S=O region. Moreover, the S–O–H bond shifts from 1131 cm^{-1} to 1040 cm^{-1} in the $\text{SO}_2/\text{D}_2\text{O}$ ice. However, these bands are not unique to sulfinothioic acid **1**, since S=O stretching vibrations overlap with those of multiple sulfur-oxygen products, including H_2SO_4 and H_2SO_3 . Accordingly, the isotope experiments strengthen the functional group assignments but do not permit unambiguous identification of a single product.^[63, 65, 67] Therefore, mass spectrometric techniques with isomer selectivity are necessary to unambiguously identify the molecular products subliming into the gas phase.

Formation Mechanism

The first pathway involves retaining the sulfur-oxygen double bond present within SO_2 ; the remaining mechanisms utilize oxygen from water to oxidize reduced sulfur species like hydrogen disulfide (H_2S_2). In the first pathway, the decomposition of SO_2 to SO and atomic oxygen (Reaction 1) can occur following interaction with high-energy electrons penetrating the ice. This decomposition is highly endoergic (+547 kJ mol^{-1}) and cannot proceed without initiation by GCRs under interstellar conditions. Similarly, H_2O can decompose into a hydrogen atom and the hydroxyl radical (OH) (Reaction 2) providing a source of suprathermal hydrogen in the ice matrix. These suprathermal hydrogen can recombine the the sulfur atom of sulfur monoxide (SO) without barrier—note that sulfur monoxide has an open shell, triplet ($^3\Pi$) electronic ground state—resulting in the formation of the hydrogen sulfinyl radical (HSO) (Reaction 3).



From this point, a source of SH atoms is required. Since hydrogen sulfide is observed in the present ice systems as well, the reaction can proceed via hydrogen loss from hydrogen sulfide (Reaction 4).



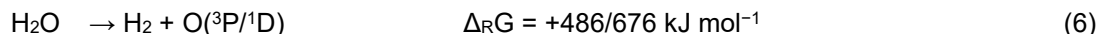
Subsequent, barrierless radical-radical recombination of the sulfinyl radical (HSO) and thiol radical (SH) can proceed producing sulfinothioic acid **1**. Although this pathway explains the signal of $m/z = 82$ in the

SO₂/H₂¹⁸O system as the route avoids ¹⁸O from H₂¹⁸O; the enhanced signal of *m/z* = 84 suggests a second pathway which utilizes oxygen from H₂¹⁸O.

Two possible routes could operate via hydrogen disulfide which could form following Reaction 4 via barrierless radical-radical recombination of two sulfinyl radicals (Reaction 5). Ab initio calculations at the CCSD(T)/aug-cc-pVTZ shows this reaction is exoergic by 240 kJ mol⁻¹.^[68]



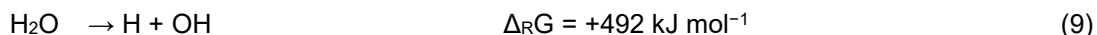
Following the formation of hydrogen disulfide, a decomposition of H₂O to atomic oxygen (Reaction 6) can occur.



Crossed-molecular beam studies of atomic oxygen addition to hydrogen sulfide (H₂S) shows ground state ³P oxygen is barrierless; however, results indicate barrierless addition to H₂S from O(¹D) resulting in the sulfenic acid (H₂SO) intermediate. Here, the results are likely reflective of these dynamics and the reaction proceeds *via* barrierless O(¹D) addition to H₂S₂ to form the sulfinothioic acid (**1**) (Reaction 7). Alternatively, suprathemal O(³P) leads to a triplet HSS(O)H intermediate which undergoes intersystem crossing to the singlet surface in the ice.



O(¹D) could also be provided by SO₂ and proceed through this route which could explain the enhanced signal at *m/z* = 82 in the SO₂/H₂¹⁸O ice. Alternatively, a second endoergic bond cleavage of an S-H bond in H₂S₂ can result in the thiosulfeno radical (HS₂) (Reaction 8). Following this, the formation of a hydroxyl radical and a hydrogen atom can proceed from water initiated by the energetic electrons (Reaction 9).



Following the endoergic cleavage in Reaction 7 and Reaction 8, the resulting thiosulfeno radical can recombine with a hydroxyl radical forming disulfanol (HSSOH, **4**) (Reaction 10).



Tautomerization of low oxidation sulfur acids is common,^[4] although the tautomerization to sulfinothioic acid **1** is endoergic; quantum tunneling of the hydrogen atom as well as initiation by GCRs could allow the tautomer to form (Reaction 11).



Given disulfanol **4** is not detected here could suggest this pathway is not dominant. Given the branching ratio reveals 67% of the oxygen retained in sulfinothioic acid **1** derives from SO₂, Pathway 1 is dominant. This process of reacting suprathemal hydrogen with SO (Reaction 3) and ending with barrierless recombination with SH produced is more efficient than Pathway 2 and 3 which incorporate oxygen from water.

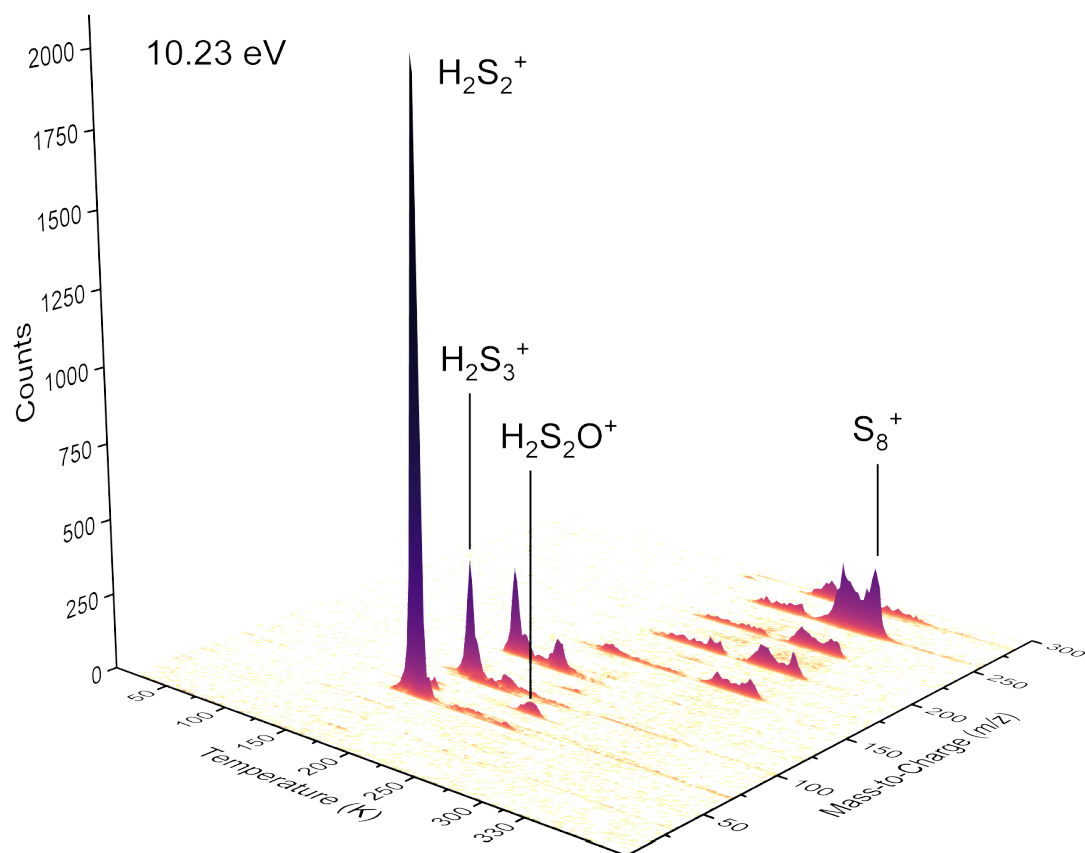


Figure S1. PI-ReToF-MS data during TPD of the sulfur dioxide-water ice after irradiation with energetic electrons. Data were recorded at 10.23 eV light revealing co-desorbing material and high mass products such as S_8^+ ($m/z = 256$).

Table S1. Experimental Parameters for each SO₂/H₂O ice. These experiments were conducted and compared with a non-irradiated SO₂/H₂O ice to ensure products derive from modification by energetic electrons.

Experiment	Ice Composition	Irradiation Current (nA)	Irradiation Time (min)	Photon Energy (eV)	Average Ice Thickness (nm)	Average Ice Ratio (SO ₂ :H ₂ O)
1	SO ₂ /H ₂ O	100	60	10.49	1280 ± 60	1 : 1.2 ± 0.2
2	SO ₂ /H ₂ O	100	60	10.23		
3	SO ₂ /H ₂ O	100	60	9.60		
4	SO ₂ /D ₂ O	100	60	10.49		
5	SO ₂ /H ₂ ¹⁸ O	100	60	10.49		
6	SO ₂ /H ₂ O	-	-	10.23		

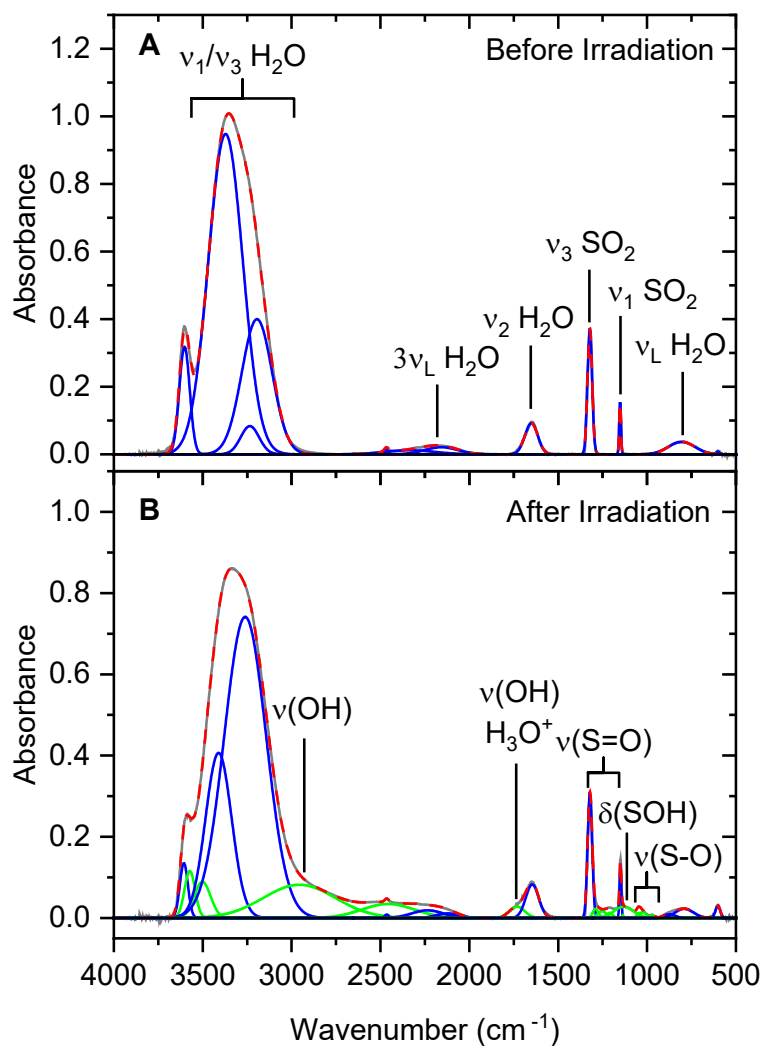


Figure S2. Fourier transform infrared spectra before (top) irradiation and after (bottom) irradiation of the $\text{SO}_2/\text{H}_2\text{O}$ ice. The infrared spectra were deconvoluted for reagents (blue) and irradiation products (green) and summed to fit (red) the original spectra (gray).

Table S2. Infrared absorption assignments of the SO₂/H₂O ice. The SO₂/H₂O ice before irradiation (left) reveals a pristine ice while after irradiation (right) shows new vibrational features.

Before Irradiation			After Irradiation		
Peak Position (cm ⁻¹)	Label	Reference	Peak Position (cm ⁻¹)	Label	Reference
3602	O-H Dangling	[43]	3606	O-H Dangling	[43]
3371	ν_1/ν_3 H ₂ O	[43]	3573	O-H Stretching	[63]
3235	ν_1/ν_3 H ₂ O	[43]	3502	O-H Stretching	[63]
3195	ν_1/ν_3 H ₂ O	[43]	3411	ν_1/ν_3 H ₂ O	[43]
2466	$\nu_1 + \nu_3$ SO ₂	[69]	3261	ν_1/ν_3 H ₂ O	[43]
2334	$3\nu_L$ H ₂ O	[43]	2957	O-H Stretching	[63]
2298	$2\nu_1$ SO ₂	[69]	2465	$\nu_1 + \nu_3$ SO ₂	[69]
2158	$3\nu_L$ H ₂ O	[43]	2456	Bound O-H Stretching	[34, 63-66]
1651	ν_2 H ₂ O	[43]	2296	$2\nu_1$ SO ₂	[69]
1322	ν_3 SO ₂	[69]	2236	$3\nu_L$ H ₂ O	[43]
1152	ν_1 SO ₂	[69]	2122	$3\nu_L$ H ₂ O	[43]
805	ν_L H ₂ O	[43]	1731	O-H Stretching H ₃ O ⁺	[63]
602	?		1646	ν_2 H ₂ O	[43]
			1322	ν_3 SO ₂	[69]
			1289	S=O asym. str.	[63]
			1253	S=O asym. str.	[63]
			1211	S=O asym. str.	[63]
			1179	S=O asym. str.	[63]
			1150	ν_1 SO ₂	[69]
			1136	S=O sym. str.	[5, 63]
			1131	S-O-H bending	[63, 65, 67]
			1047	S-O stretching	[63]
			1025	S-O stretching	[63]
			972	S-O stretching	[63]
			949	S-O stretching	[63]
			873	ν_L H ₂ O	[43]
			790	ν_L H ₂ O	[43]
			602	?	

Table S3. Parameters for the generation of VUV light utilizing difference four-wave mixing. The resulting photon energy has an uncertainty of less than 0.001 eV.

Experiment	Medium	ω_{VUV}	ω_1 (nm)	YAG 1 Wavelength (nm)	ω_1 Dye	YAG 2 Wavelength (nm)	ω_2 (nm)	ω_2 Dye	Energy (eV)
1	Xenon	$3\omega_1$	355 ^a	355	-	-	-	-	10.49
2	Krypton	$2\omega_1 - \omega_2$	202.316	532	Rhodamine 610/640	532	845.71	LDS 863	10.23
3	Krypton	$2\omega_1 - \omega_2$	202.316	532	Rhodamine 610/640	355	466.72	Coumarin 460	9.60

^aNd:YAG harmonic/fundamental

Table S4. Calculated CCSD(T)-F12/cc-pVTZ-F12 (F12-TZ) adiabatic ionization energies (IE, eV) and relative energies (kJ mol⁻¹) for H₂S₂O isomers.

Identity	Formula	Relative Energy (kJ mol⁻¹)	Adiabatic IE (eV)
1a	HSS(O)H	59.0	9.91
1b	HSS(O)H	64.6	9.85
2a	HSOSH ^a	123.0	9.15
2b	HSOSH ^a	123.4	9.15
3a	HS(S)OH	66.4	9.02
3b	HS(S)OH	72.1	8.91
4a	HSSOH ^a	0.0	8.98
4b	HSSOH ^a	1.8	8.97

^aOnly one cation conformer is present for this connectivity.

Table S5. H₂S₂O isomers with CCSD(T)-F12/cc-pVTZ-F12 optimized geometries in Å and energy in Hartree.

2a⁺, 2b⁺

ENERGY=-871.49169819

S	0.0000000000	0.1072782757	-1.4574593778
O	0.0000000000	-0.6125412711	-0.0107632246
S	0.0000000000	0.1848100540	1.4290925575
H	0.0000000000	-0.9679777703	2.1258602463
H	0.0000000000	1.4004846312	-1.0527354603

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2b

ENERGY=-871.82842915

O	-0.7055345571	0.0682700807	0.0000000000
S	0.1590876461	-0.0557598362	1.4278082320
H	0.5394317740	1.2317401686	1.5120727832
S	0.1590876461	-0.0557598362	-1.4278082320
H	0.5394317740	1.2317401686	-1.5120727832

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2a

ENERGY=-871.82854829

O	0.0000000000	-0.0000000000	0.7116229304
S	-1.4278238918	-0.0408059517	-0.1617786992
H	-1.4717131133	1.2592264399	-0.5021577271
S	1.4278238918	0.0408059517	-0.1617786992
H	1.4717131133	-1.2592264399	-0.5021577271

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4a

ENERGY=-871.87858704

S	0.5927955182	0.0006761975	-0.5345176274
S	-0.2014185187	-0.0443816120	1.3252584467
H	-0.3708940192	1.2759679930	1.5200566148
O	-0.6977964171	0.0602766169	-1.5720853110
H	-1.0014323194	-0.8426030263	-1.7172200777

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4a⁺, 4b⁺

ENERGY=-871.54742371

S	0.5898392658	-0.0129447204	-0.5463015041
S	-0.1586186914	0.0153749561	1.3004851277
H	-1.3619563100	-0.4642740708	0.9082825378
O	-0.7442675077	0.0317446651	-1.4196824507
H	-0.5400398920	-0.1169201979	-2.3618011728

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4b

ENERGY=-871.87791980

S	0.5918665402	0.0137918816	-0.5342273616
S	-0.2017025903	-0.0465006233	1.3257273854

H	-0.3624868926	1.2720424182	1.5409770989
O	-0.6956149776	-0.0669847613	-1.5741179342
H	-1.0058822194	0.8316128096	-1.7300243508

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1a⁺

ENERGY=-871.49325628

S	-0.3915474621	0.0894750976	-0.5766196775
S	0.1168302934	-0.0434567249	1.3732850619
H	1.2230825278	0.7122826250	1.1787613086
H	-1.4085862226	-0.8260441525	-0.5996632371
O	0.5621716453	-0.0850459539	-1.6328605031

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1a

ENERGY=-871.85434450

S	-0.4582602100	0.0632607475	-0.6360422362
S	0.1466573087	-0.0474695934	1.3876764149
H	0.2934360656	1.2817327964	1.4871685012
H	-0.9643492022	-1.1997195142	-0.4593100736
O	0.6666643251	-0.0368094345	-1.5708971207

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3a⁺

ENERGY=-871.52212026

S	-0.0437211096	-0.5096377958	-0.4836623983
S	0.0020990197	0.2040084248	1.3513517223
O	-0.0339430070	0.5953227515	-1.6096133710
H	0.6462861680	1.2837310666	-1.5125585855
H	1.2163960853	-1.0122160909	-0.5364438932

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3a

ENERGY=-871.85422040

S	-0.0445499612	-0.5519803748	-0.4614947767
S	0.0030619239	0.2178680432	1.3115474428
O	-0.0218087440	0.6419139155	-1.5868334408
H	0.4322913748	1.3995572821	-1.1863414733
H	1.2335154162	-0.9616305696	-0.6632780683

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3b⁺

ENERGY=-871.52407642

S	-0.0591717587	-0.5120057020	-0.4767225402
S	0.0060274387	0.2071716939	1.3482071491
O	0.0795996337	0.6241338369	-1.5808121488
H	-0.7710155407	0.7816939217	-2.0256887634
H	1.1978867031	-0.9928062991	-0.6012043732

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3b

ENERGY=-871.85201915

S	-0.0633656732	-0.5384649833	-0.4370649346
S	0.0130209086	0.2270377480	1.3256047178
O	0.0759262083	0.6195428833	-1.6253864689
H	-0.8019573746	1.0057836952	-1.7392081773
H	1.1980914451	-0.9343084535	-0.7226220666

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1b⁺

ENERGY=-871.49325630

S	-0.0894561701	-0.3915902607	-0.5765998118
S	0.0434465592	0.1168421208	1.3732236134
H	-0.7121399778	1.2231068440	1.1784082609
H	0.8258938179	-1.4088060696	-0.5998820102
O	0.0850288809	0.5622460243	-1.6327411546

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1b

ENERGY=-871.85195478

S	-0.0331181615	-0.4655420300	-0.6388846147
S	-0.0389838437	0.1314120783	1.3911042407
H	1.1406151279	0.7708423473	1.3503886776
H	1.2570895528	-0.9036499115	-0.5179114642
O	-0.0065722570	0.6779046908	-1.5597615093

Table S6. Frequencies (cm⁻¹) of the H₂S₂O isomer with geometries optimized at the CCSD(T)-F12/cc-pVTZ-F12 level of theory

2a

181.03	265.34	309.98	649.88	781.41
1014.90	1015.65	2657.65	2659.29	

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2b

211.39	250.86	317.01	652.63	774.70
1015.68	1026.50	2649.99	2653.84	

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2a⁺, 2b⁺

207.85	262.69	294.64	516.04	643.64
1038.81	1086.55	2596.81	2661.66	

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4a

281.39	401.29	431.82	527.65	767.75
901.46	1191.40	2647.15	3793.23	

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4b

283.59	400.80	435.87	529.05	767.68
903.15	1190.81	2642.74	3794.29	

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4a⁺, 4b⁺

187.29	247.20	306.57	582.07	845.69
888.67	1169.62	2616.78	3668.64	

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1a⁺

317.49	437.03	681.47	829.22	967.98
1096.59	2021.91	2488.44	2619.42	

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1a

250.36	315.60	446.88	757.28	910.55
1074.46	1162.19	2445.44	2689.37	

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1b⁺

318.19	440.45	685.11	827.29	968.09
1099.32	2020.25	2488.52	2620.39	

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1b

280.60	312.23	463.80	738.21	996.55
1086.28	1168.32	2422.95	2700.83	

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3a⁺

275.04	361.48	494.92	717.15	870.57
977.35	1159.82	2554.72	3694.59	

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3a

251.53	392.25	633.88	742.71	906.97
1012.82	1184.98	2510.08	3710.62	

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3b⁺

250.83	315.22	494.83	715.09	860.17
999.11	1218.81	2604.75	3702.61	

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3b

204.10	305.43	649.88	713.57	872.33
1017.28	1234.95	2553.11	3783.43	

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Table S7. Simulated vibrational modes and strengths of sulfinothoic acid (HSS(O)H) and its isotopologues—HSS(¹⁸O)H and DSS(O)H. These simulated spectra consist of the anharmonic vibrational modes including the fundamentals, overtones, and combination bands along with their peak positions and intensity (km mol⁻¹).

HSS(O)H

Fundamental Bands

Mode(n)	E(anharm)	I(anharm)
1(1)	2556.6	0.886956
2(1)	2250.985	55.30783
3(1)	1107.594	169.8433
4(1)	1023.211	4.567066
5(1)	932.216	3.083679
6(1)	697.495	4.297338
7(1)	414.961	50.27263
8(1)	341.622	3.148805
9(1)	176.612	11.36548

Overtones

Mode(n)	E(anharm)	I(anharm)
1(2)	5010.461	0.546093
2(2)	4404.275	0.634324
3(2)	2200.428	2.87455
4(2)	2030.822	0.546857
5(2)	1856.985	0.170507
6(2)	1391.027	0.093276
7(2)	826.268	0.106653
8(2)	527.965	0.27297
9(2)	496.236	0.287286

Combination Bands

Mode(n)	Mode(n)	E(anharm)	I(anharm)
2(1)	1(1)	4805.638	0.01438
3(1)	1(1)	3664.323	0.01905
3(1)	2(1)	3362.875	0.507799
4(1)	1(1)	3578.581	0.074195
4(1)	2(1)	3256.639	0.16854
4(1)	3(1)	2124.889	0.239172
5(1)	1(1)	3481.83	0.207697
5(1)	2(1)	3173.424	0.032442
5(1)	3(1)	2037.981	0.081299

5(1)	4(1)	1952.173	0.009958
6(1)	1(1)	3244.847	0.121563
6(1)	2(1)	2939.64	0.274173
6(1)	3(1)	1804.217	0.062136
6(1)	4(1)	1718.176	0.019737
6(1)	5(1)	1618.495	0.166815
7(1)	1(1)	2971.242	0.015075
7(1)	2(1)	2666.992	0.022629
7(1)	3(1)	1522.854	0.012105
7(1)	4(1)	1435.593	0.170376
7(1)	5(1)	1342.773	0.019218
7(1)	6(1)	1109.964	0.179063
8(1)	1(1)	2824.801	0.018309
8(1)	2(1)	2519.549	0.027412
8(1)	3(1)	1373.981	0.062509
8(1)	4(1)	1289.559	0.032628
8(1)	5(1)	1194.861	0.072572
8(1)	6(1)	963.344	0.169862
8(1)	7(1)	678.391	0.51539
9(1)	1(1)	2806.887	0.007417
9(1)	2(1)	2500.831	0.006003
9(1)	3(1)	1356.64	0.025435
9(1)	4(1)	1272.182	0.055328
9(1)	5(1)	1177.08	0.08093
9(1)	6(1)	951.328	2.645843
9(1)	7(1)	660.533	0.602364
9(1)	8(1)	511.241	0.579492

HSS(¹⁸O)H

Fundamental Bands

Mode(n)	E(anharm)	I(anharm)
1(1)	2553.46	0.896338
2(1)	2250.044	55.26918
3(1)	1062.914	171.7944
4(1)	1021.093	3.191295
5(1)	931.01	3.225249
6(1)	697.164	4.567989
7(1)	413.811	50.19139
8(1)	339.132	3.162844
9(1)	168.066	11.10998

Overtones

Mode(n)	E(anharm)	I(anharm)
1(2)	5004.181	0.545411
2(2)	4402.262	0.633955
3(2)	2107.468	3.177558
4(2)	2026.609	0.521522
5(2)	1858.361	0.168569
6(2)	1390.827	0.098348
7(2)	823.778	0.097504
8(2)	518.239	0.289518
9(2)	483.696	0.325667

Combination Bands

Mode(n)	Mode(n)	E(anharm)	I(anharm)
2(1)	1(1)	4801.547	0.014368
3(1)	1(1)	3616.521	0.019517
3(1)	2(1)	3317.74	0.513549
4(1)	1(1)	3573.284	0.074233
4(1)	2(1)	3252.807	0.168498
4(1)	3(1)	2077.363	0.242466
5(1)	1(1)	3479.292	0.207925
5(1)	2(1)	3172.346	0.032374
5(1)	3(1)	1993.843	0.076168
5(1)	4(1)	1951.167	0.009621
6(1)	1(1)	3241.5	0.121498
6(1)	2(1)	2938.299	0.274206
6(1)	3(1)	1759.61	0.063771
6(1)	4(1)	1716.494	0.019434
6(1)	5(1)	1621.228	0.169046
7(1)	1(1)	2966.95	0.015096
7(1)	2(1)	2664.905	0.022659
7(1)	3(1)	1478.242	0.011578
7(1)	4(1)	1432.377	0.175486
7(1)	5(1)	1342.222	0.02392
7(1)	6(1)	1108.346	0.075644
8(1)	1(1)	2814.112	0.018629
8(1)	2(1)	2513.852	0.028683
8(1)	3(1)	1324.854	0.066545
8(1)	4(1)	1282.709	0.032817
8(1)	5(1)	1191.278	0.056211
8(1)	6(1)	959.148	0.243178

8(1)	7(1)	672.499	0.456432
9(1)	1(1)	2794.247	0.007756
9(1)	2(1)	2493.557	0.006847
9(1)	3(1)	1306.992	0.026886
9(1)	4(1)	1263.723	0.049562
9(1)	5(1)	1173.785	0.067487
9(1)	6(1)	944.777	1.961861
9(1)	7(1)	653.124	0.443246
9(1)	8(1)	500.106	0.640826

DSS(O)D

Fundamental Bands

Mode(n)	E(anharm)	I(anharm)
1(1)	1858.674	0.491957
2(1)	1641.615	29.70802
3(1)	1108.479	176.4924
4(1)	757.444	1.427566
5(1)	701.621	5.491697
6(1)	507.662	2.744617
7(1)	419.703	31.31775
8(1)	269.773	2.292977
9(1)	186.776	8.984368

Overtones

Mode(n)	E(anharm)	I(anharm)
1(2)	3664.312	0.217093
2(2)	3233.045	0.236453
3(2)	2201.733	2.77236
4(2)	1507.402	0.253852
5(2)	1396.917	0.092484
6(2)	1014.37	0.159054
7(2)	835.887	0.088566
8(2)	534.225	0.015157
9(2)	362.977	18.37401

Combination Bands

Mode(n)	Mode(n)	E(anharm)	I(anharm)
2(1)	1(1)	3499.257	0.005822
3(1)	1(1)	2967.259	0.013881
3(1)	2(1)	2753.288	0.352725

4(1)	1(1)	2615.683	0.006643
4(1)	2(1)	2389.477	0.053245
4(1)	3(1)	1861.333	0.088566
5(1)	1(1)	2556.354	0.100647
5(1)	2(1)	2338.223	0.008459
5(1)	3(1)	1808.968	0.030118
5(1)	4(1)	1457.071	0.032899
6(1)	1(1)	2361.971	0.044033
6(1)	2(1)	2145.99	0.103204
6(1)	3(1)	1616.305	0.025906
6(1)	4(1)	1262.675	0.022955
6(1)	5(1)	1204.66	0.034492
7(1)	1(1)	2278.078	0.010347
7(1)	2(1)	2061.607	0.012692
7(1)	3(1)	1528.503	0.008697
7(1)	4(1)	1176.758	0.178003
7(1)	5(1)	1116.931	0.066128
7(1)	6(1)	924.438	0.017885
8(1)	1(1)	2126.292	0.004743
8(1)	2(1)	1909.418	0.024259
8(1)	3(1)	1374.145	0.083593
8(1)	4(1)	1022.504	0.022804
8(1)	5(1)	966.84	0.029448
8(1)	6(1)	776.366	0.44039
8(1)	7(1)	685.082	0.105446
9(1)	1(1)	2047.76	0.013998
9(1)	2(1)	1830.352	0.005969
9(1)	3(1)	1296.646	0.014422
9(1)	4(1)	946.884	0.038097
9(1)	5(1)	885.71	0.092964
9(1)	6(1)	698.16	0.689869
9(1)	7(1)	622.285	0.037365
9(1)	8(1)	453.128	0.307468

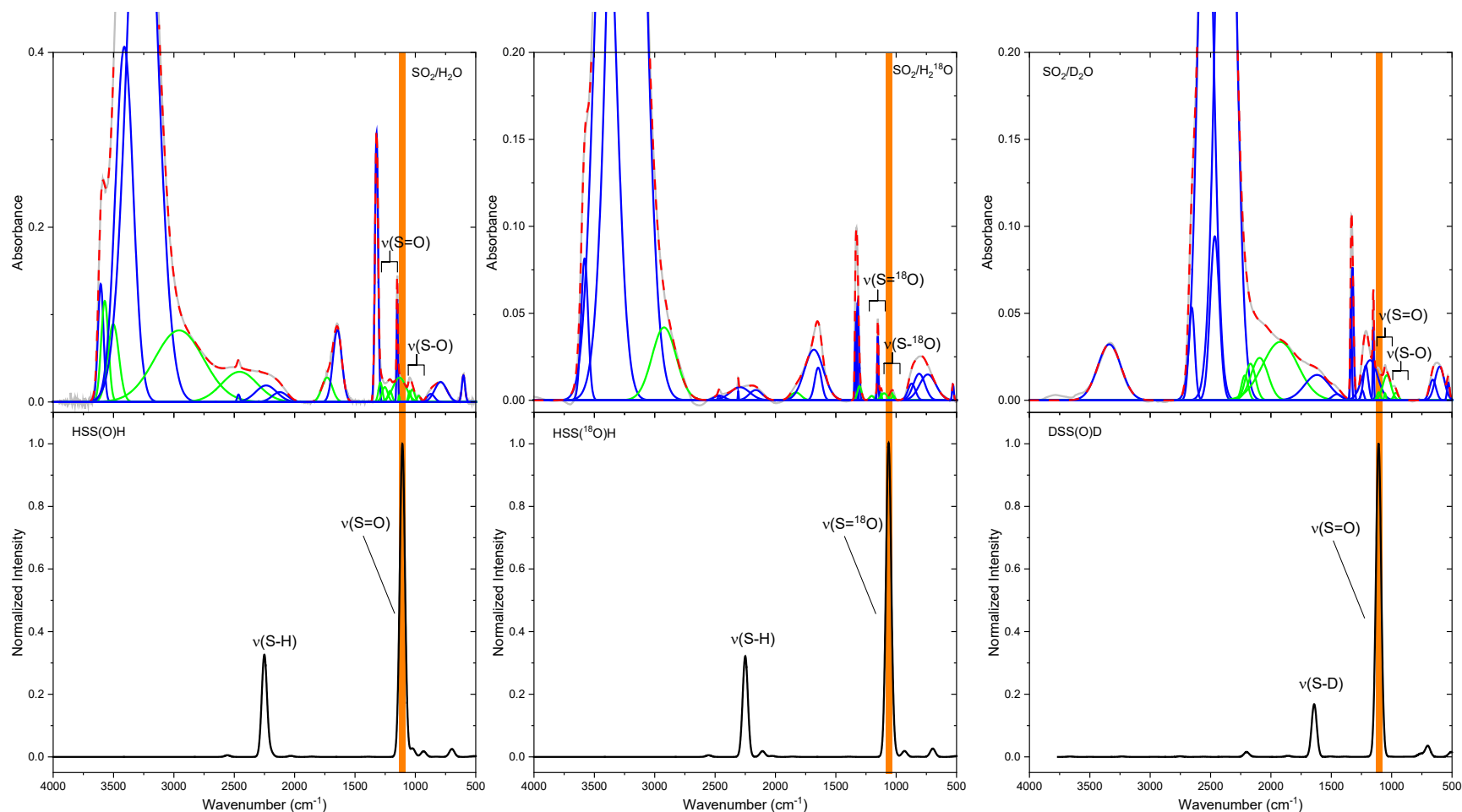


Figure S3. Fourier transform infrared spectra of the $\text{SO}_2/\text{H}_2\text{O}$ ices after irradiation (top), compared with the calculated anharmonic vibrational spectra of the sulfinic acid ($\text{HSS}(\text{O})\text{H}$, **1**) (bottom). The isotopically labeled ices— $\text{SO}_2/\text{H}_2^{18}\text{O}$ and $\text{SO}_2/\text{D}_2\text{O}$ —are directly compared with the isotopically labeled variants of sulfinic acid— $\text{HSS}^{(18}\text{O})\text{H}$ and $\text{DSS}(\text{O})\text{D}$. Each irradiated spectra (top) has been deconvoluted to show the original spectra (gray), the fitted spectra (red dashed), peaks associated with reagents (blue), and new vibrational modes derived from irradiation (green).

Table S8. Peaks observed in the FTIR spectra of the irradiated SO₂/H₂¹⁸O ice.

Peak Position (cm ⁻¹)	Label	Reference
3581	ν_1/ν_3 H ₂ ¹⁸ O dangling	[43]
3413	ν_1/ν_3 H ₂ ¹⁸ O	[63]
3230	ν_1/ν_3 H ₂ ¹⁸ O	[63]
2922	¹⁸ O-H Stretching	[63]
2466	$\nu_1 + \nu_3$ SO ₂	[69]
2465	Bound $\nu(^{18}\text{O-H})$ str.	[34, 63-66]
2308	$2\nu_1$ SO ₂	[69]
2294	$3\nu_L$ H ₂ ¹⁸ O	[43]
2163	$3\nu_L$ H ₂ ¹⁸ O	[43]
1831	O-H Stretching H ₃ O ⁺	[63]
1681	ν_2 H ₂ ¹⁸ O	[43]
1646	ν_2 H ₂ ¹⁸ O	[43]
1338	ν_3 SO ₂	[69]
1330	ν_3 SO ₂	[69]
1319	ν_3 SO ₂	[69]
1304	S=O assym. str.	[63]
1203	S=O assym. str.	[63]
1173	S=O assym. str.	[63]
1152	ν_1 SO ₂	[69]
1150	ν_1 SO ₂	[69]
1125	S= ¹⁸ O assym. str.	[5, 63]
1099	S- ¹⁸ O-H bending	[63, 65, 67]
1039	S-O stretching	[63]
1022	S-O stretching	[63]
872	ν_L H ₂ ¹⁸ O	[63]
809	ν_L H ₂ ¹⁸ O	[63]
739	ν_L H ₂ ¹⁸ O	[43]
530	ν_2 SO ₂	[69]

Table S9. Peaks observed in the FTIR spectra of the irradiated SO₂/D₂O ice.

Peak Position (cm ⁻¹)	Label	Reference
3338	ν_1/ν_3 HDO	[70]
2656	ν_1/ν_3 D ₂ O	[70]
2541	ν_1/ν_3 D ₂ O	[70]
2465	ν_1/ν_3 D ₂ O	[70]
2373	ν_1/ν_3 D ₂ O	[70]
2216	$\nu(\text{O-D})$ str.	[71]
2169	$\nu(\text{O-D})$ str.	[71]
2094	$\nu(\text{O-D})$ str.	[71]
1923	Bound $\nu(\text{O-D})$ str.	[63]*
1618	$3\nu_L$ D ₂ O	[70]
1452	ν_2 HDO	[70]
1336	ν_3 SO ₂	[69]
1325	ν_3 SO ₂	[69]
1243	ν_2 D ₂ O	[70]
1215	ν_2 D ₂ O	[70]
1178	ν_2 D ₂ O	[70]
1152	ν_2 SO ₂	[69]
1141	ν_2 SO ₂	[69]
1107	S=O assym. str.	[63]
1055	S=O sym. str.	[63]
1040	S-O-D bending	[63, 65, 67]
977	S-O stretching	[63]
964	S-O stretching	[63]
659	ν_L D ₂ O	[70]
603	ν_L D ₂ O	[70]
531	ν_2 SO ₂	[69]

*estimated

Table S10. Diagnostic peak positions for sulfinothioic acid **1** (HSS(O)H) based on B3LYP/aug-cc-pVTZ anharmonic vibrations and their respective intensity (cm molecule⁻¹). These peaks are compared with emerging peaks close in peak position to the diagnostic peaks chosen for sulfinothioic acid **1**.

SO ₂ /H ₂ O: HSS(O)H				
Mode	Peak Position (cm ⁻¹)	Band Strength (cm molecule ⁻¹)	Label	Peak After Irradiation (cm ⁻¹)
v ₂	2251	9.2×10^{-18}	S-H stretching	n.d.
v ₃	1108	2.8×10^{-17}	S=O stretching	1136, 1131
SO ₂ /H ₂ ¹⁸ O: HSS(¹⁸ O)H				
Mode	Peak Position (cm ⁻¹)	Band Strength (cm molecule ⁻¹)	Label	Peak After Irradiation (cm ⁻¹)
v ₂	2250	9.2×10^{-18}	S-H stretching	n.d.
v ₃	1063	2.9×10^{-17}	S= ¹⁸ O stretching	1086, 1045
SO ₂ /D ₂ O: DSS(O)D				
Mode	Peak Position (cm ⁻¹)	Band Strength (cm molecule ⁻¹)	Label	Peak After Irradiation (cm ⁻¹)
v ₂	1642	4.9×10^{-18}	S-D stretching	n.d.
v ₃	1108	2.9×10^{-17}	S=O stretching	1108

Note. n.d. is not detected.